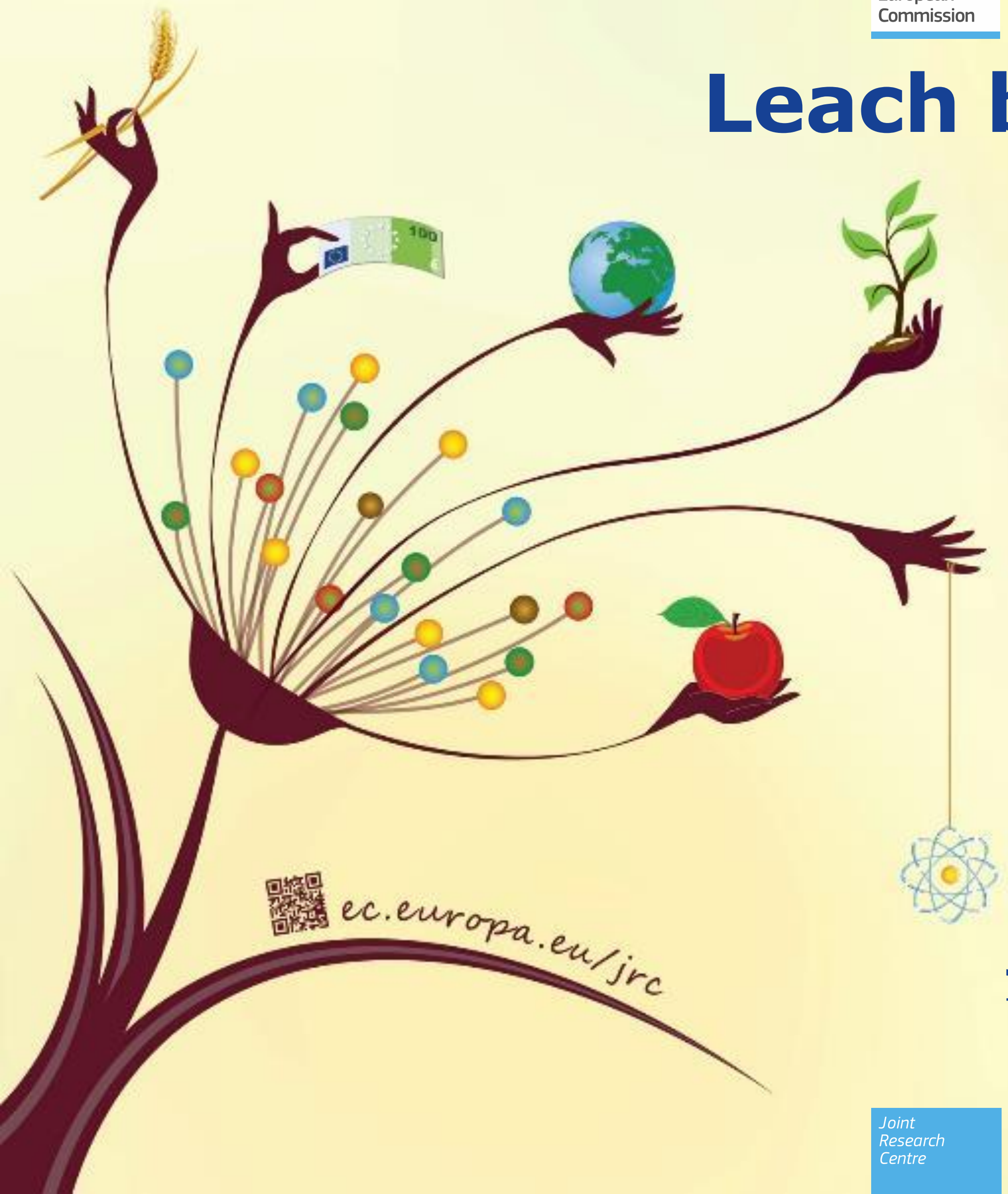
Leach behavior of corium

Daniel Serrano Purroy



Joint ICTP-IAEA International School on Nuclear Waste Actinide Immobilization
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Joint Research Centre
the European Commission's
in-house science service

Outline of presentation

- ☐ What happens during a Nuclear core-melt accidents?
  - ☐ **TMI-2**
  - ☐ **ChNPP4**
  - ☐ **1F**
- ☐ What is corium?
  - ☐ **Formation of corium**
  - ☐ **Composition**
- ☐ Corium Management strategies
- ☐ How can we estimate the long-term stability of corium?
  - ☐ **SNF alteration mechanism**
  - ☐ **IRF**
  - ☐ **Matrix dissolution**
- ☐ Leach experiments
  - ☐ **Case studies**
- ☐ Outlook

What happens during a Nuclear Core-Melt Accident?

- Three Mile Island
- Chernobyl
- Fukushima

What happens during a Nuclear Core-Melt Accident?

***Cooling capacity is lost** in an operating or recently shutdown nuclear reactor*

***Heat** generated by radioactive decay*

***Melting of the reactor core**, including nuclear fuels*

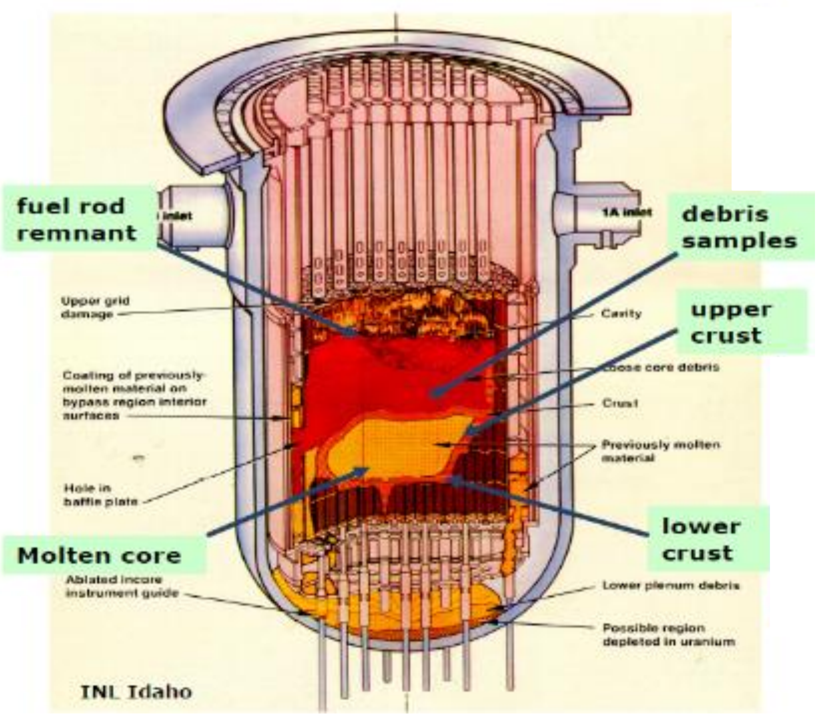
*Since early 1950s about 20 core-melt accidents. The most recent and dramatic ones occurred at operating nuclear power plants: **TMI-2**, **ChNPP4** and **1F**.*

*Each one was very **different** in its scale and the **conditions experienced by the fuel** before and after the accident.*

Three Mile Island (TMI-2)

*28 March 1979: prolonged Loss of Coolant Accident (**LOCA**) in PWR.*

Half of the core damaged, 20 metric tons of melted fuel, failure of about 20% of the fuel cladding.



INL Idaho

Damaged/molten irradiated fuel remained inside of the RPV. No dispersion of particulates.

No MCCI. "In-vessel corium".

Several phases of corium: oxidic phase and metallic phases.

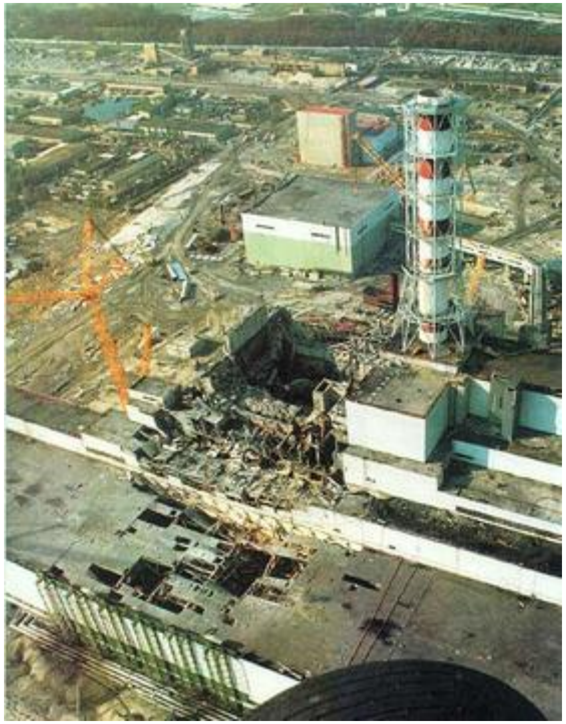
Defueling completed in early 1990.

***Solution:** Fuel and debris properly stored in Idaho DoE facilities.*

Chernobyl (ChNPP4)

26 April 1986: catastrophic power increase leading to explosions in its core and open-air fire. Destroyed graphite-moderated reactor.

Dispersion of large quantities of radioactive isotopes into the atmosphere (no proper containment vessel).



Fission gases (e.g. Kr and Xe) and volatile fission products (e.g. I and Cs) were released.

Dispersion of about 6t of fuel as air-borne particles.

About 190t of the core damaged or melted.

In vessel and ex-vessel corium(MCCI).

Chernobyl (ChNPP4)

*Formation of **lava**, consisting of melted fuel assemblies, structural material such as concrete and steel, and sand and boric acid added to control criticality and reduce the release of radionuclides.*

$$U_xZr_{1-x}SiO_4$$

***Solution:** Shelter confinement, "Sarcophagus".*

Alkaline water with high carbonate concentrations.

Fukushima Daiichi nuclear accident (1F)

11 March 2011: Magnitude 9.0 (Richter) Tohoku Earthquake.

Tsunami caused loss of reactor coolant.

Four reactors destroyed:

- **R1-3 operating at the time of the earthquake (256t). Mainly UO_2 but some MOX in R3 (5.5t)**
- **R4, fuel removed and stored in neighbouring pool**
- **R1-R4 storage tanks (461t of irradiated and unirradiated UO_2)**

Fukushima Daiichi nuclear accident (F1)

Failed cooling systems in the BWR reactors (Units 1-3) resulted in:

- **Compromised irradiated fuel**
- **Partial to complete melting of the cores**
- **H_2 explosions in four units**
- **Release of radionuclides**

Damaged/molten irradiated fuel and large quantities of seawater and boric acid water were brought together.

***Large amounts of salt** may have deposited in the reactor cores.*

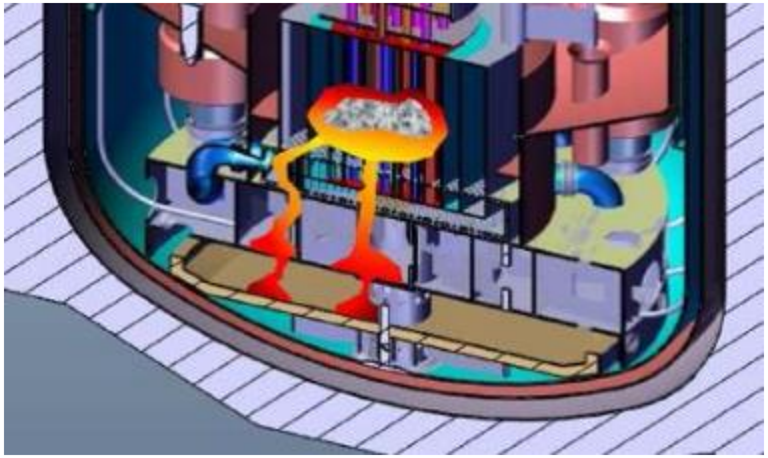
Solution: several management strategies being discussed.

What is Corium?

- ☐ Definition
- ☐ Formation
- ☐ Composition

What is Corium?

In case of a severe nuclear accident, the core of the reactor can melt forming corium !!!



Consists of:

- ☐ **nuclear fuel**
- ☐ **fission products**
- ☐ **control rods**
- ☐ **structural materials**
- ☐ **products of their chemical reaction with air, water and steam**

The composition depends on the design and type of the reactor.

*In the event that the reactor vessel is breached the corium will react with molten concrete from the floor of the reactor room causing a molten core concrete interaction (**MCCI**) and the formation of ex-vessel corium*

Formation of Corium

Stages of core-melt incident:

- *800°C melting of Ag-In-Cd absorber*
- *750-1100°C deformation and bursting of fuel cladding*
- *1200°C steam oxidation of structural and fuel rod materials*
- *1300°C eutectic interactions of cladding with stainless steel*
- *1450°C melting of stainless steel*
- *1500°C interactions of cladding with UO_2 fuel*
- *1760°C melting of cladding*
- *2690°C melting of ZrO_2*
- *2850°C melting of UO_2*

High release during core-melt: *B.J. Lewis et al. (2012)*
Pontillon and Ducros (2010)

- *Volatile fission products, up to 90% of Cs, I, FG…*
- *Semi-volatile fission products, up to 50% of Mo, Tc..*
- *Low-volatility fission products <1% Sr, Ru, Ce…*
- *Non-volatile radionuclides: U, An, Zr, Nd…*

Composition (radiotoxicity)

Irradiated UO_2 fuels

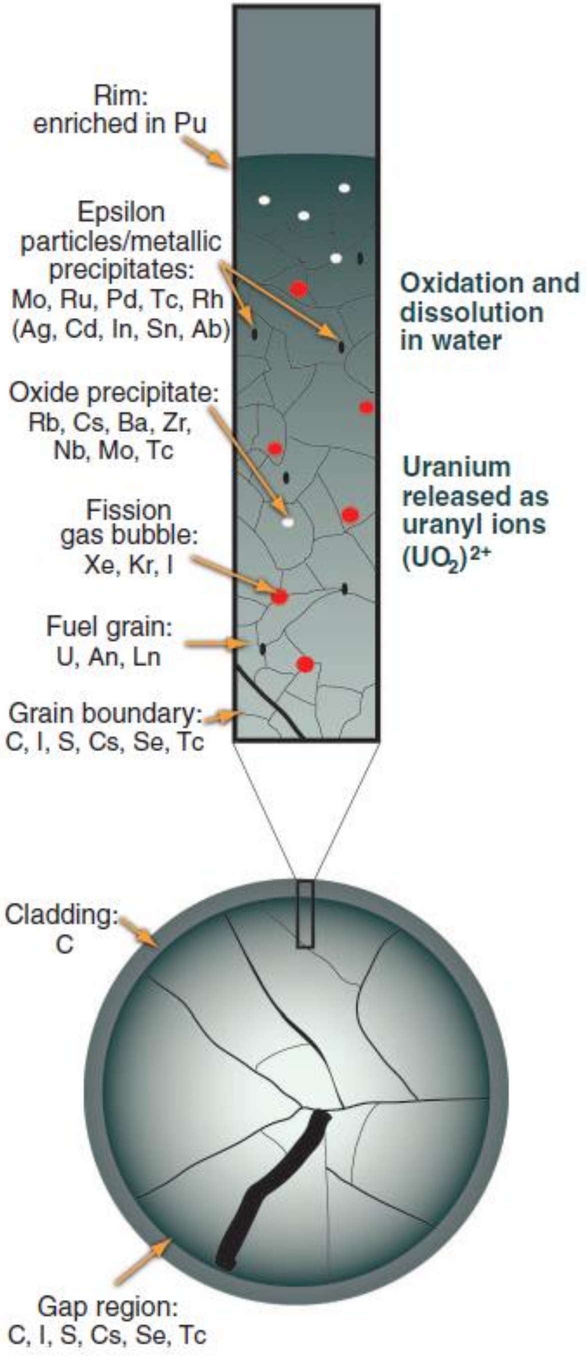
- *>95% UO_2*
- *Fission gases (Xe, Kr…) in bubbles within grains*
- *Metallic FP (Mo, Tc, Ru, Pd, Rh…) as immiscible ε-particles*
- *Oxide precipitates (Rb. Cs. Ba, Zr…)*
- *In solid solution within the matrix (Sr, Zr, Nb, lanthanides, actinides)*

Thermal gradient

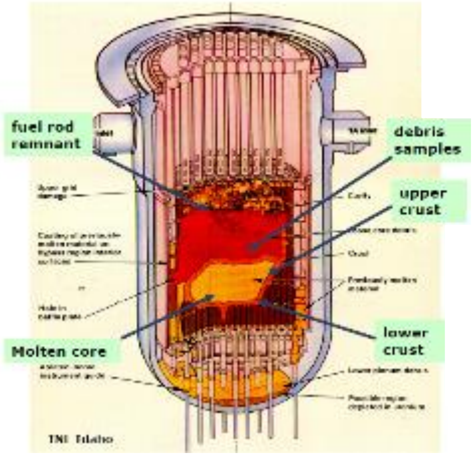
- *Heterogeneous distribution (I, Cs…)*

Non-uniform burn-up

- *Higher Pu concentrations near the pellet edge*



Composition (TMI-2 samples)



Conditions during accident

1) Max. Temperature

- Edge of reactor	T < 800°C
- Agglomerate	T~1500°C (stainless st. mp)
- fully molten core	T= 2000-2500°C
(some pure UO_2 seen	T=2850°C?)

2) Cool-down

core	- slow (2-54 h)
Agglomerate	- more rapid & variable
Edge of core	- transient rise in temp.; only slight degradation

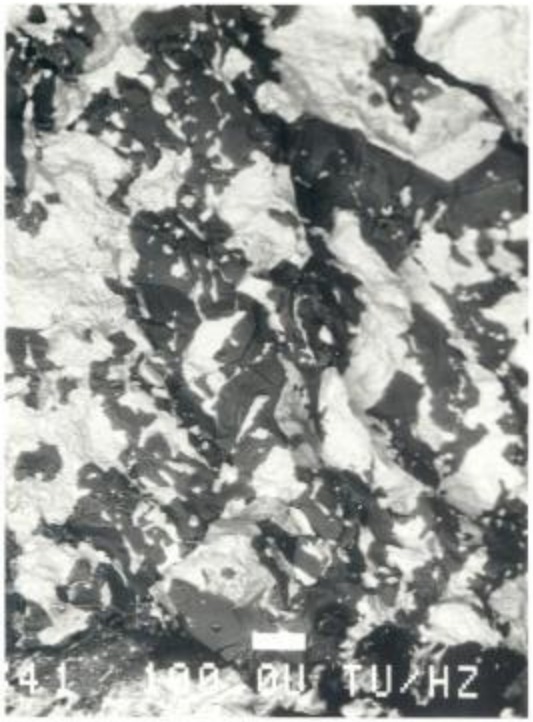
3) Oxygen potential during the accident is estimated at -150kJ/mol ($p_{H_2}/p_{H_2O} = 1$) at 2000°C to -510kJ/mol O_2 ($p_{H_2}/p_{H_2O} = 10^6$) for 1200°C. Suggests high H_2 presence could be possible at times.

Composition (TMI-2 samples)

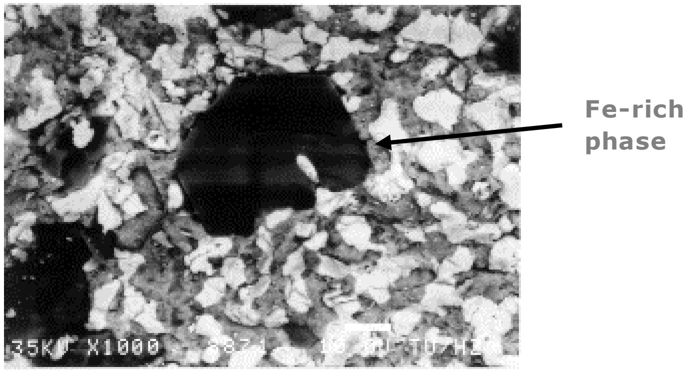
Phases formed

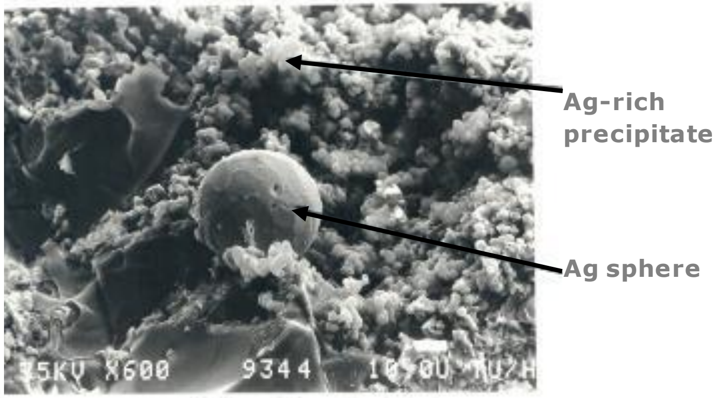
Core: a UO_2 fuel & Zry cladding melt that oxidised in steam generating H_2 and formed a U,Zr-containing oxide. The core also contained small amounts of Fe,Ni,Cr oxides & Ag nodules.

a) Secondary Electron Image



b) Back-scattered Electron Image





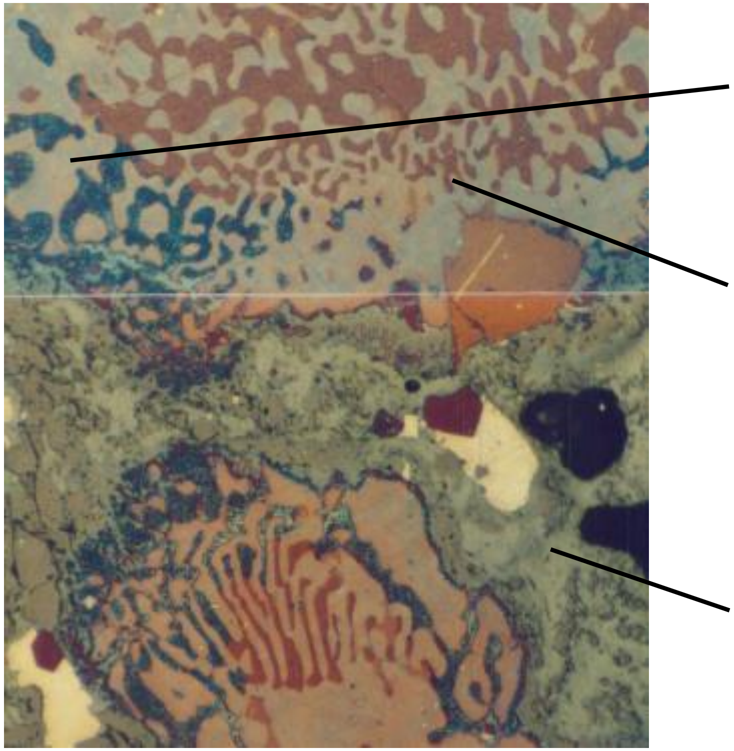
c) Silver Sphere Precipitate

U-rich phase (white)
Ze-rich phase (dark)

Composition (TMI-2 samples)

Phases formed

Agglomerate: mixed metallic and ceramic phases from fuel/cladding/structure interactions (often incomplete) eg. $(U,Zr)O_2$ phases, (Fe,Ni)-Zr-U oxides, Ni-Fe-Sn metal, Ni,Fe partially oxidised nodules, & Ag metal nodules



2 phase metallic/oxidic zone

2 phase metallic zone

Oxidic zone with some secondary precipitates

Interference micrograph (190x)

Corium Management Strategies

Corium Management Strategies

1. *Recovery and condition in suitable containers* ***TMI-2*** ***(ca. 30t)***
   - ☐ Higher alteration rate than that of the spent nuclear fuel
   - ☐ Lower Instant Release Fraction that dominates the long-term impact in a repository
2. *Treatment to reduce radiotoxicity*
   - ☐ *Hydrochemistry*
   - ☐ *Pyrochemistry*
3. *Protective sarcophagus* ***ChNPP4*** ***(ca. 200t)***
   - ☐ Probable corium corrosion and release
   - ☐ Temporary solution, up to hundreds of years

Corium Management Strategies

In any case, only a preliminary estimation of the long-term performance is possible based on the present knowledge of spent nuclear fuel

Studies of real corium samples are needed !!!

Either to develop a treatment process or to characterise the radionuclide release

*In the absence of relevant and **robust data**, conservative assumptions in performance assessment will lead to prohibitively expensive solutions*

How can we estimate the long-term stability of corium?

- ☐ SNF alteration mechanism
  - ☐ Instant Release Fraction
  - ☐ Matrix Dissolution
  - ☐ Secondary Phase Formation

How can we estimate the long-term stability of corium?

Oxic corium is a solid solution with a tetragonal structure

Can be considered as hyperstoichiometric UO_{2+x}

Bottomley et. al (1989)	*TMI-2*	$x=0.14$
Barrachin et. al (2008)	*PHEBUS*	$x=0.33$

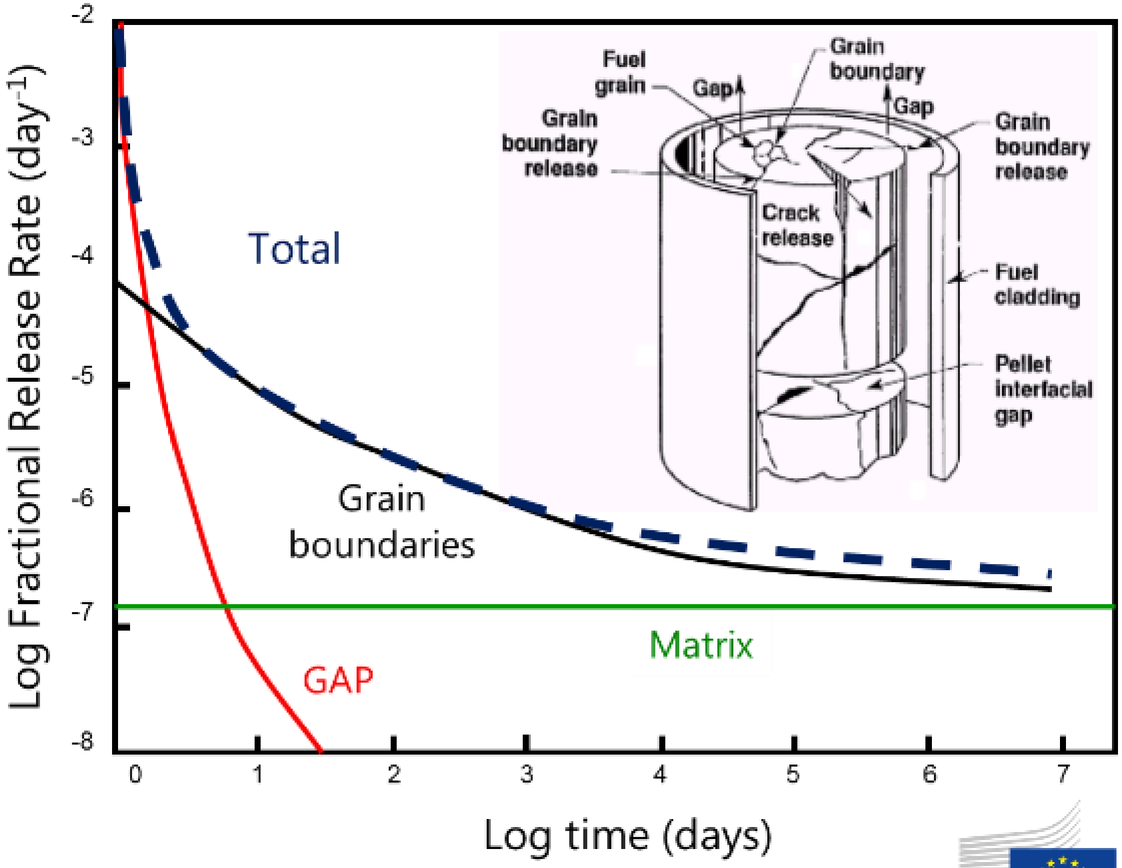
>30y worldwide studies on different types of uranium oxides (UO_{2+x}*: partly oxidised or fresh spent nuclear fuel, alpha-doped* UO_2*, oxidised* UO_2*, pure* UO_2 *and natural uraninite) to assess the the long-term behaviour of spent nuclear fuel under geological repository conditions*

Analogy to the Spent Nuclear Fuel !!!

SNF alteration mechanism

Two main alteration mechanisms

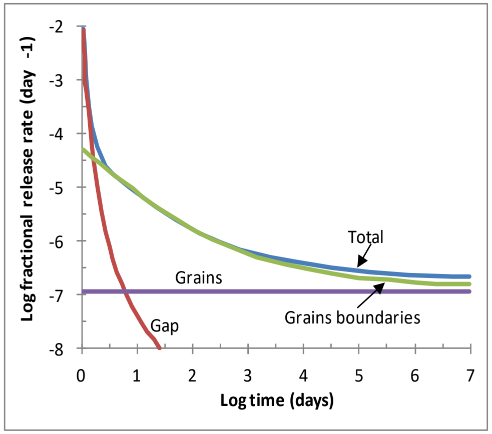
1. *Instant Release Fraction (IRF)* *"Fast" Release*
2. *Matrix dissolution* *Slow Release*



Instant Release Fraction

SNF

- Instant Release Fraction (IRF) is considered to govern the dose arising from the repository
- Contribution from the grain boundaries and void spaces (gap, cracks…)
- Same order of magnitude as FGR. Values between 0.1 and 20%, typically 3-5%



Corium

- Very high temperature (>2300°C)
- Direct contact with cooling waters

Remaining IRF in the corium anticipated to be very limited!!!

Matrix dissolution

Two competing mechanisms, electrochemically controlled:

1. *Under **oxidising conditions***

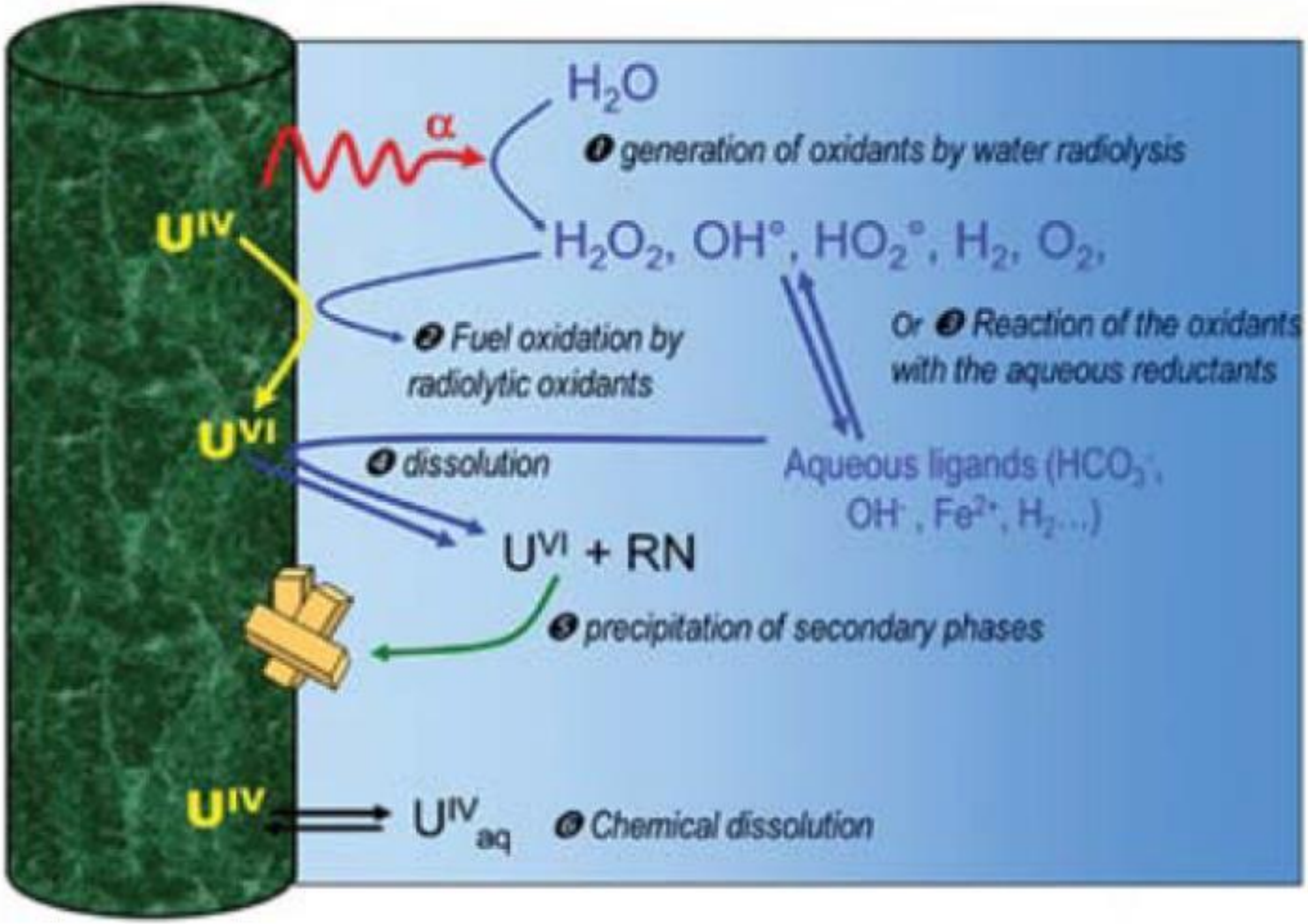
   - ☐ *Relatively fast surface-interaction-controlled dissolution*
   - ☐ ***Corium:** Anticipated to be a **faster oxidation rate** than for spent nuclear fuel as corium is likely to be already oxidised (x=0,33)*

2. *Under **reducing conditions***

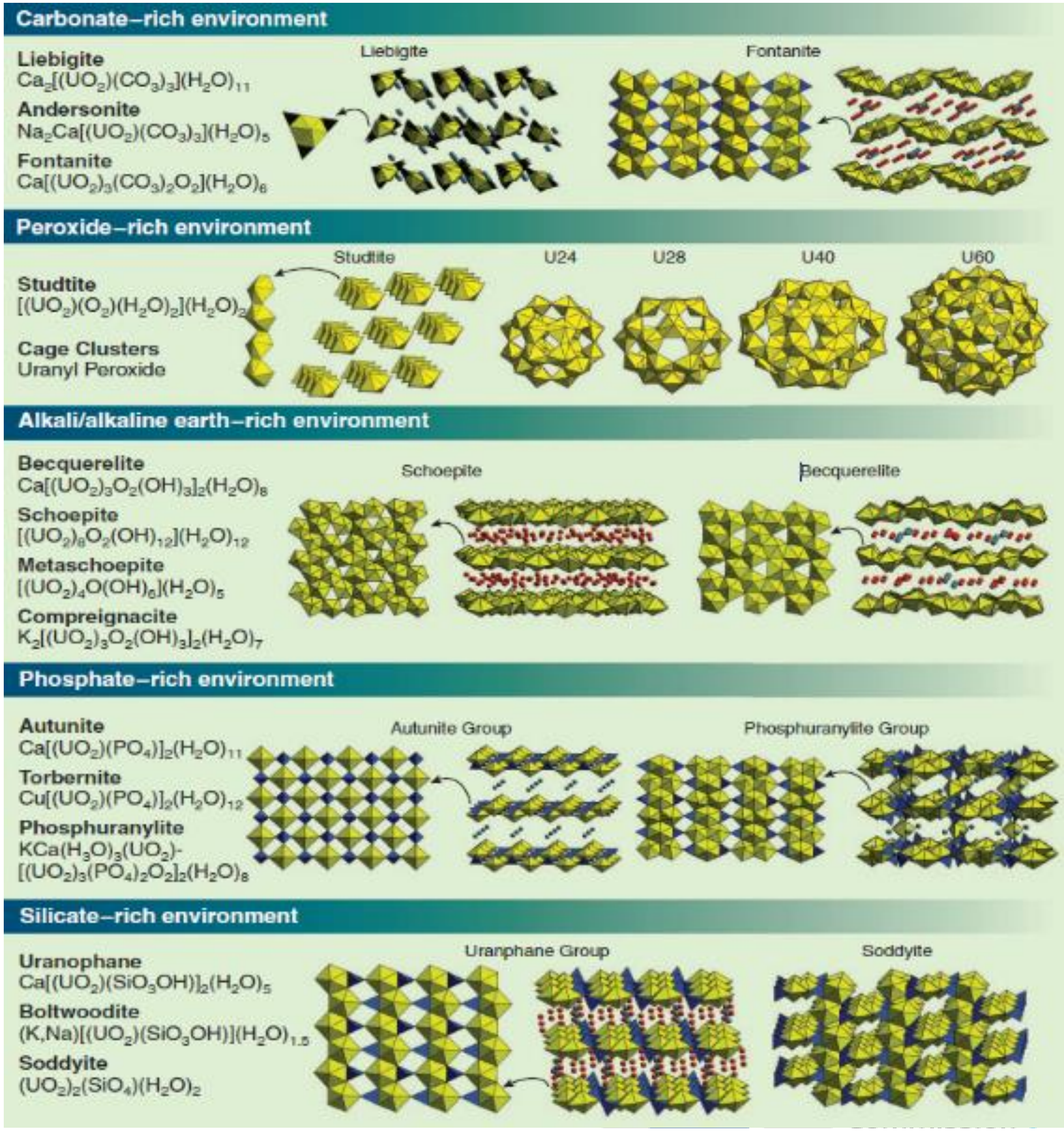
   - ☐ *Slow solubility-controlled dissolution*

   - ☐ *Corium: solubility will depend on its actual chemical state but might be higher than for spent nuclear fuel*

Matrix dissolution



Interaction of irradiated fuel and corium with groundwater and emergency cooling waters cab lead to the formation of ***secondary phases***

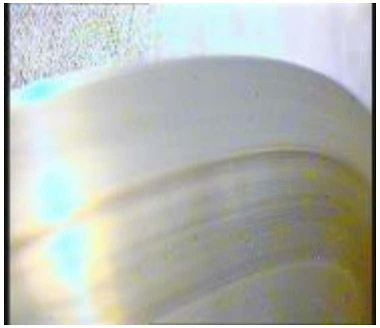


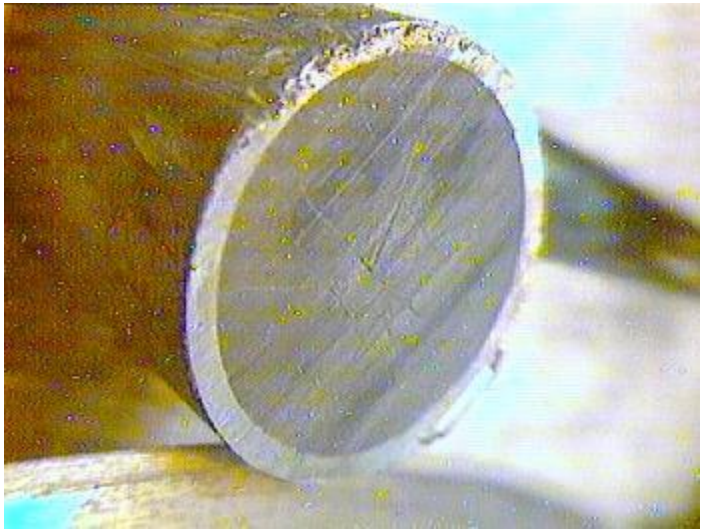
Leach experiments

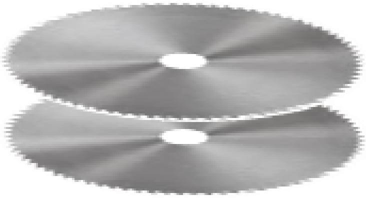
- Case studies
  - Experiments with SNF in 1F post-accidental conditions
  - Experiments with TMI-2 core samples

Experiments with Spent Nuclear Fuels

Sample name	54BWR	60PWR
Reactor	BWR	PWR
BU GWd $(t_{HM})^{-1}$	54	60
FGR (%)	3.9	13.6
LPD (W cm^{-1})	160	250







No dishing effect

Experimental

Leaching solutions and sampling

- Deionized water (WAT)
- Simulated ground water (BIC)
  - **1mM NaHCO3 + 19mM NaCl**
- Boric acid water (BOR)
  - **2g/L HBO_3**
- Seawater (SEA)
  - **Pacific Ocean (Japan)**
  - **Simulated**

	Concentration seawater (ppm)	Concentration simulated seawater (ppm)
Na	10600	10500
K	350	30
Ca	370	530
Mg	1200	2700
Cl	17500	23000
C	26	-
Br	68	64
CO_3^-	110	140
B	4	5
F	1	1
SO_4^{2-}	2300	2600
Cs	-	-
Sr	6	22
TOC	**5**	**<0,005**
pH	8.0	8.2

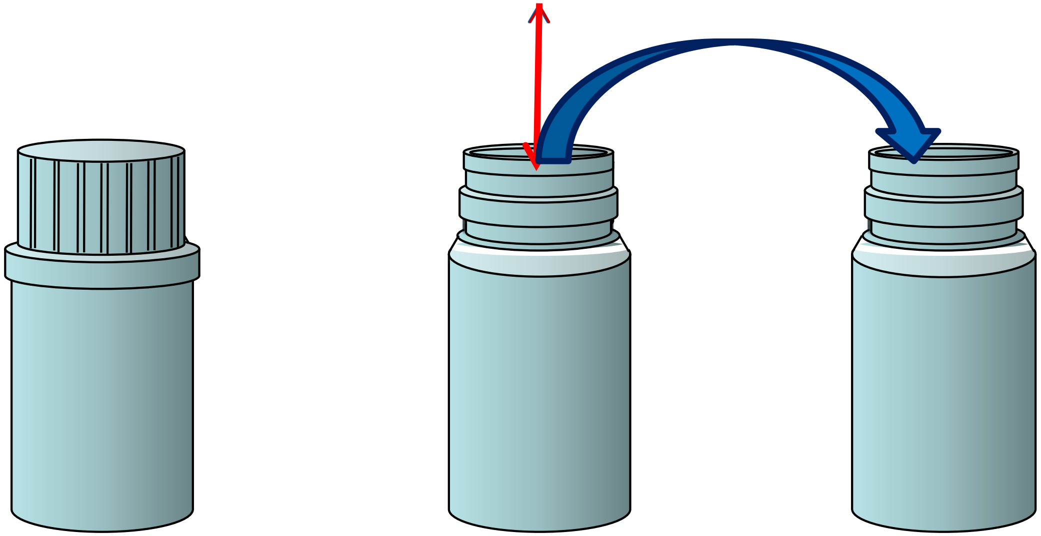
Experiment label	54WAT	54SEA	54BIC	60WAT	60BOR	60SEA	60BIC
Length (mm)	2.2	1.8	2.5	2.8	2.7	3.0	4.3
SNF weight (g)	1.17	1.01	1.64	1.37	1.47	1.41	2.62
Leaching solution	WAT	SEA	BIC	WAT	BOR	Sim SEA	BIC

Experimental

Corrosion experiments

- *Gas phase: air, oxidising condition*
- *Volume: 50±1 mL*
- *Temp: 25±5 °C*
- *Duration: 150-300 days*
- *PE-bottles with PEEK sample holder*
- *Sampling: complete replenishments*

Matrix corrosion and IRF



3 mL in HNO_3 media

50 mL HNO_3 2M

9 mL in HNO_3 media

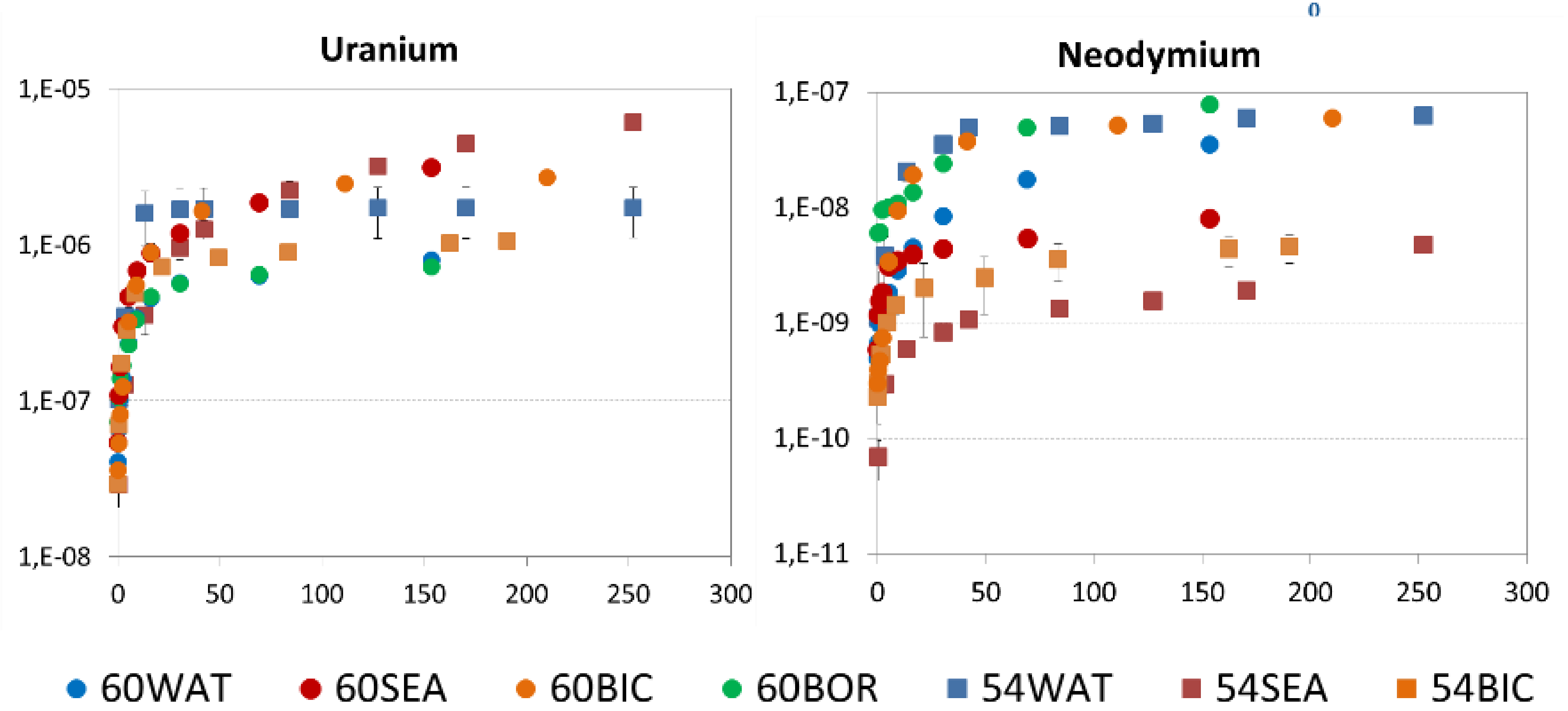
46 mL

ICPMS Sampling

Results and discussion

Cumulative moles vs time (days)

$$cummoles(i) = \sum_{0}^{n} moles_{sample}(n,i)$$



Higher Uranium release in seawater

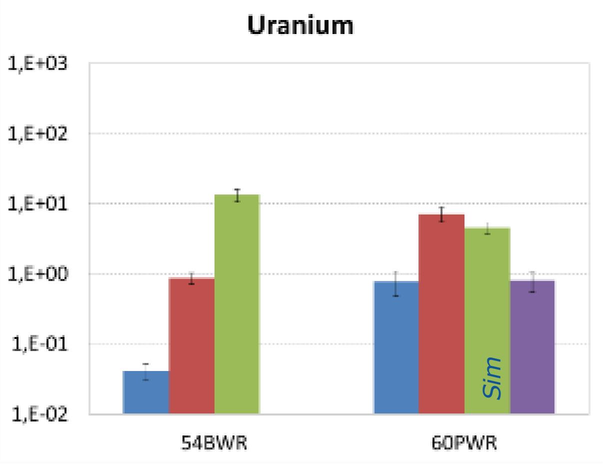
Lower Nd, Am and Pu release in seawater

Indication of U secondary phase formation

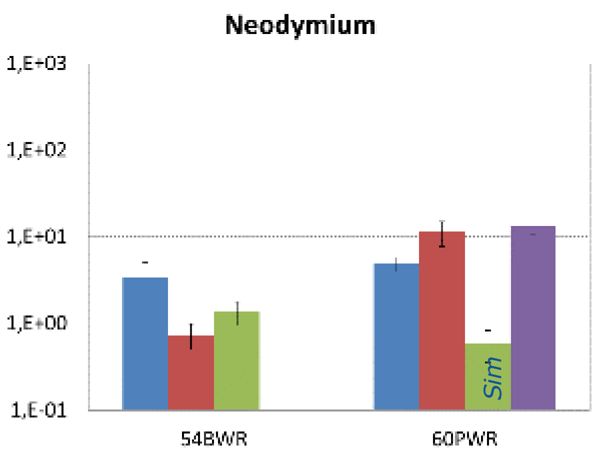
Results and discussion

Long-term dissolution rates (mg/m^2 d)

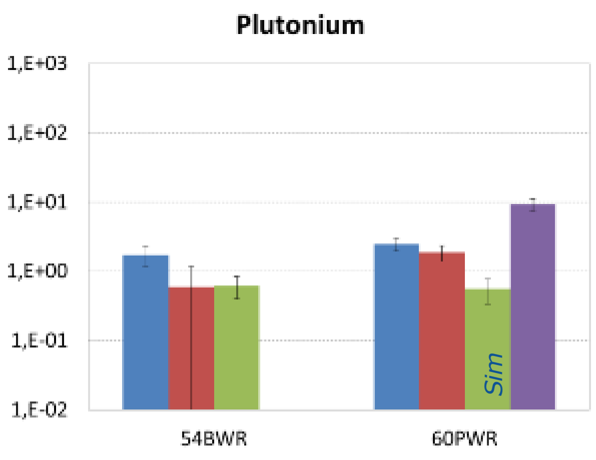
$$r_{nor}(i) = \frac{\Delta Cummoles(i) \times H_u}{\Delta t \times S \times H_i}$$



Uranium

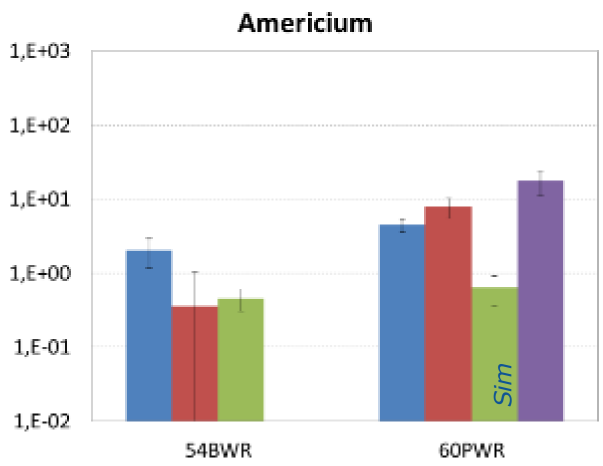


Neodymium

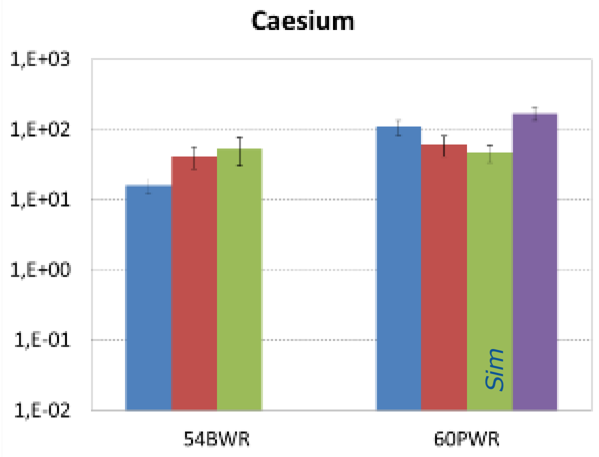


Plutonium

🟦 WAT 🟥 BIC 🟩 SEA 🟪 BOR



Americium



Caesium

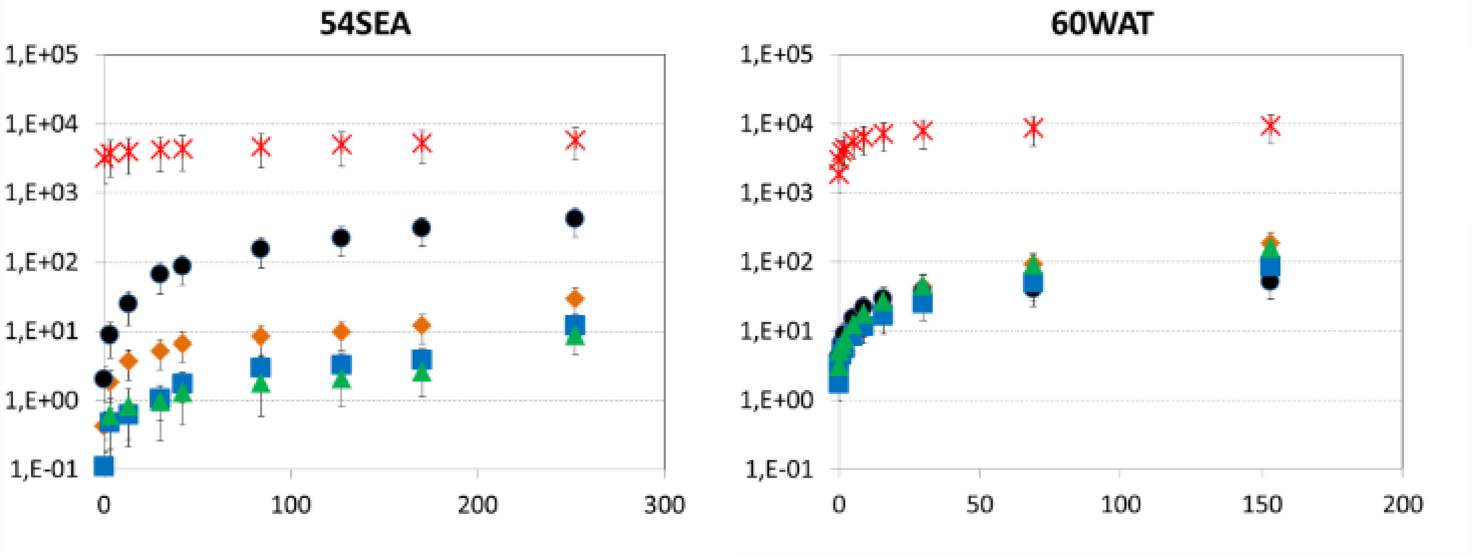
Normalised "matrix" uranium dissolution rate (mg/m^2d)	
54WAT	0.04±0.01
54BIC	0.9±0.2
54SEA	13±3
60WAT	0.8±0.3
60BIC	7±2
60SEA	5±1
60BOR	13±3

BOR≈SEA>Simulated SEA≈BIC>WAT

Results and discussion

Cumulative FIAP (%) g m^{-2} vs time (days)

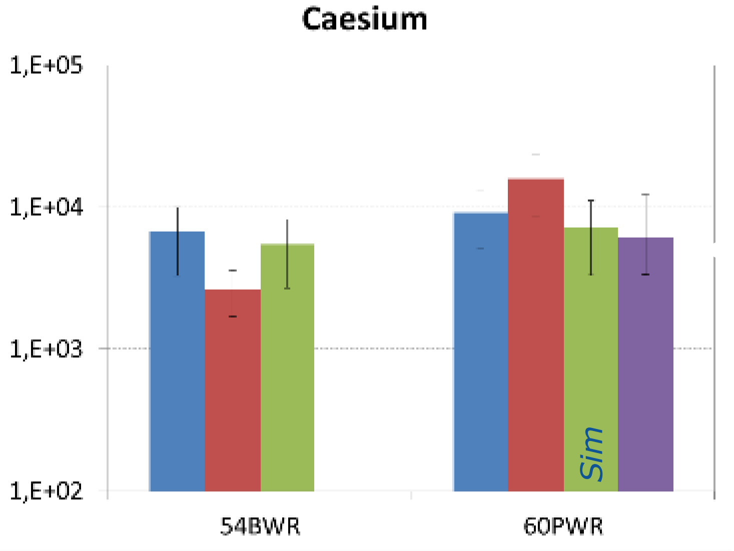
$$CumFIAP_i = \frac{m_{i,aq}}{SS \times m_{SNF} \times H_i}$$



Significant Cs release

IRF (%) g m^{-2} vs time (days)

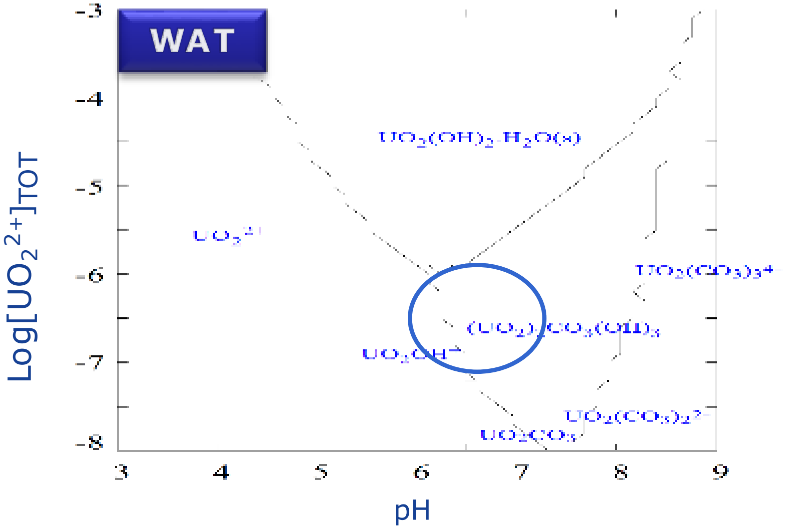
$$IRF_i = CumFIAP_i - CumFIAP_U$$

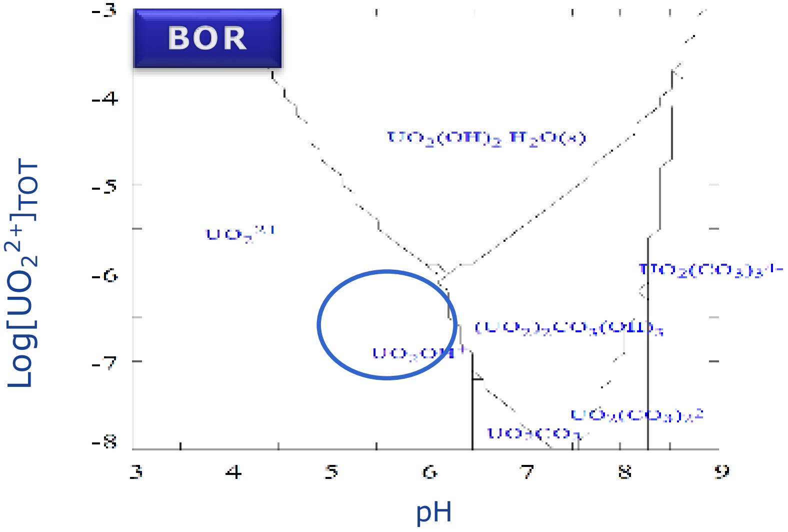


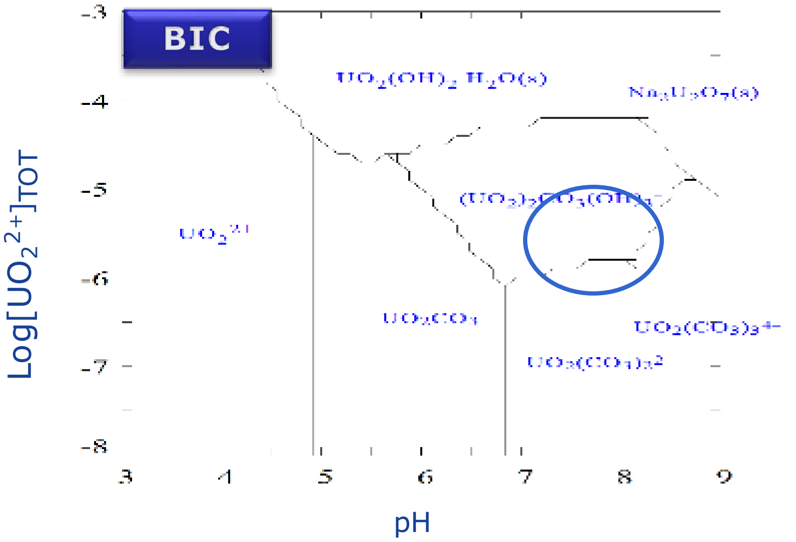
No significant differences between studied aqueous media

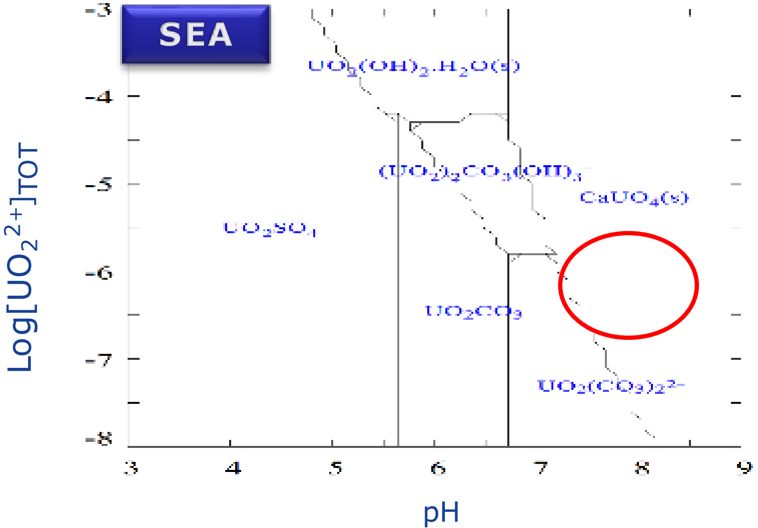
Results and discussion

Speciation studies: log(UO_2^{2+}) vs pH





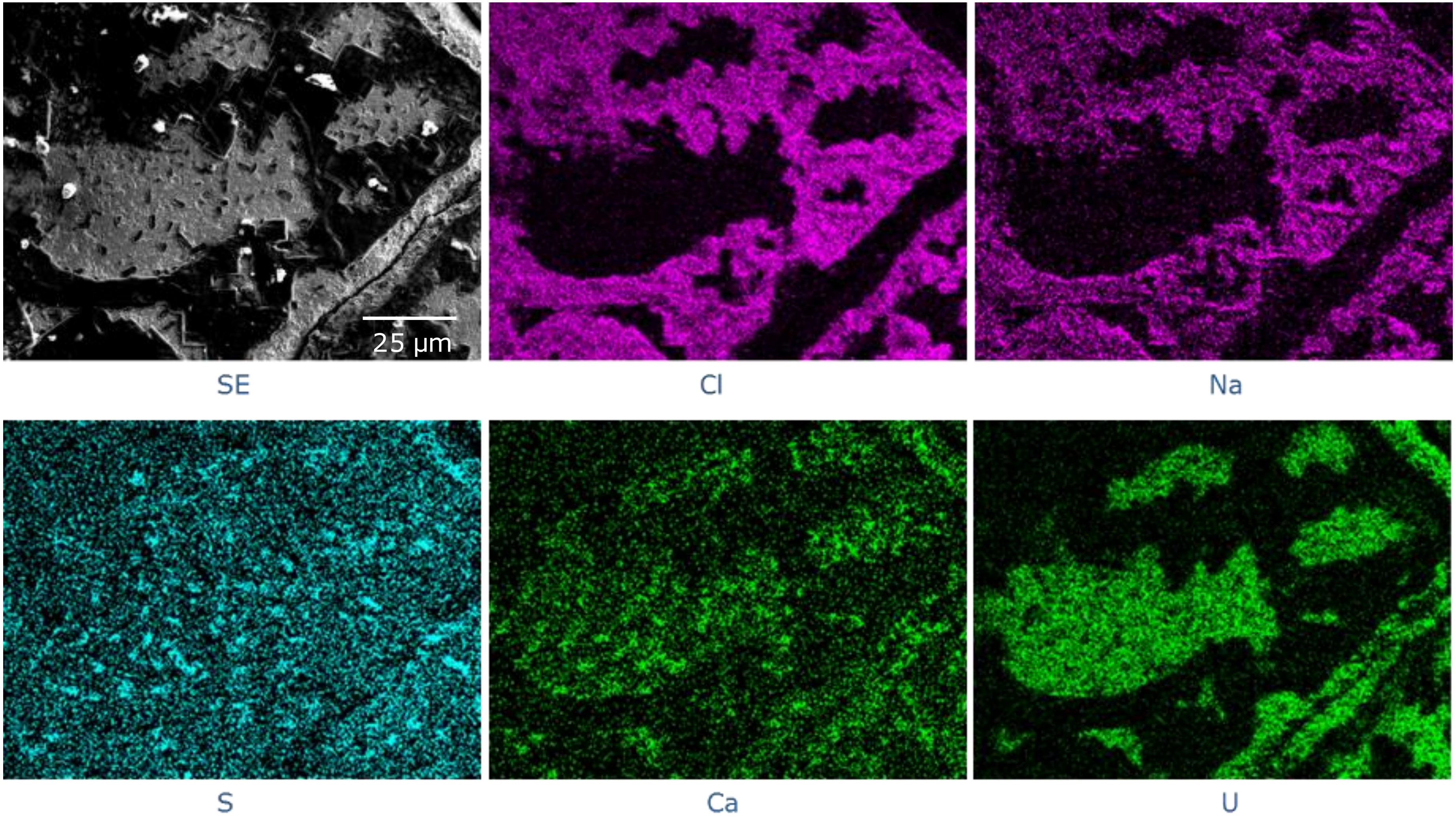




Results and discussion

SEM EDX: Secondary phase formation in seawater

54SEA



NaCl and $CaUO_4$ deposits

Conclusions

***Corrosion** in seawater and boric acid water is higher than in groundwater, with the exception of highly mobile species like caesium which show similar release in all aqueous media.*

BOR≈SEA>Simulated SEA≈BIC>WAT

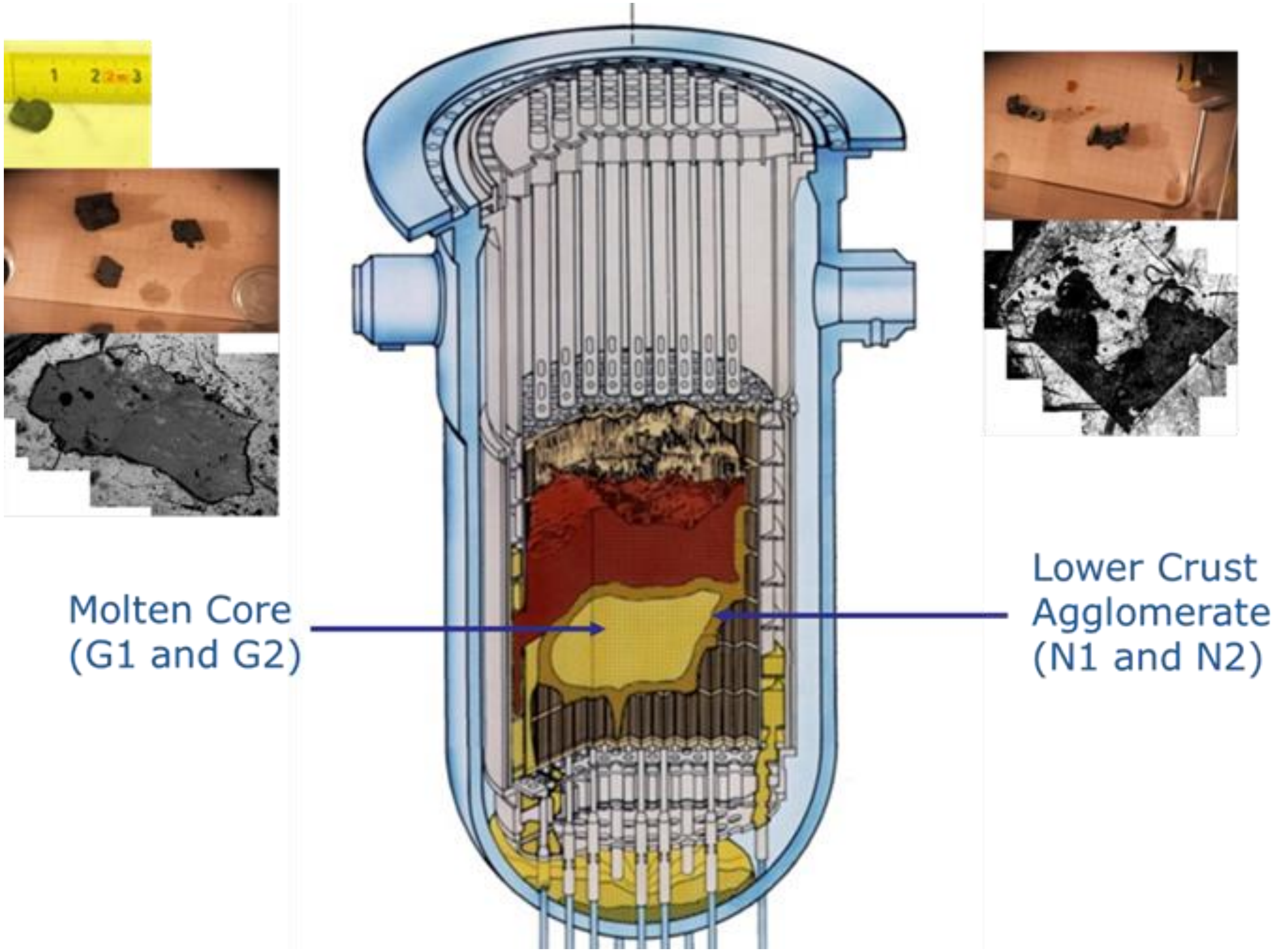
Corrosion in "real" seawater higher than in "simulated" seawater.

Secondary phase $CaUO_4$ *is formed in seawater starting at* 10^{-7} *M.*

The results are consistent with reported spent fuel corrosion data and assist for the remediation processes of the Fukushima Daichii site.

Further work will investigate relevant mechanisms governing this corrosion process.

Experiments with TMI-2 core samples



Molten Core
(G1 and G2)

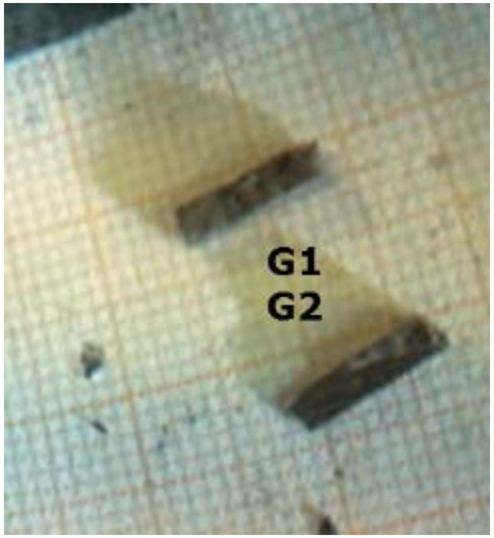
Lower Crust
Agglomerate
(N1 and N2)

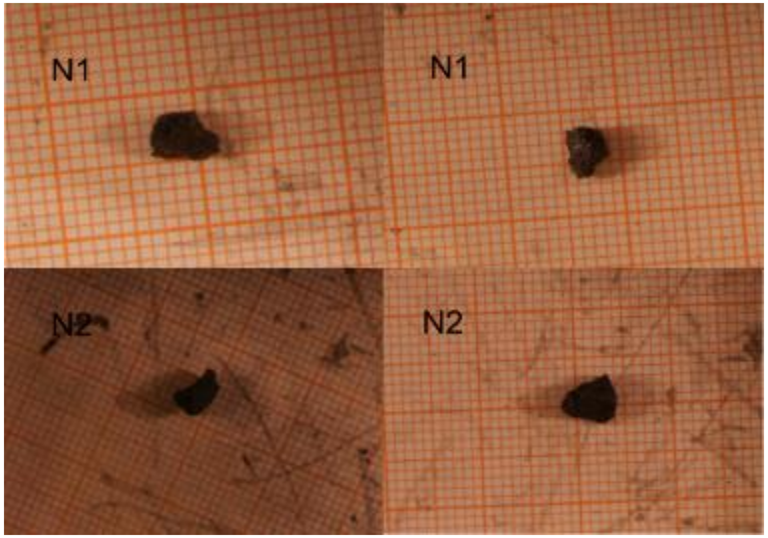
Samples from late 80's from a former OECD international collaboration on debris characterisation

Experimental

Experiment label	**G1**	**G2**	**N1**	**N2**
Approx. SNF x,y dimensions (mm)*	8x2x2	8x2x2	5x5x4	5x4x4
SNF weight (g)	0.15	0.14	0.20	0.28
Leaching solution	Deionized water	Boric acid 2g/L	Deionized water	Boric acid 2g/L
V leaching sol. (mL)	50	50	50	50

** Based on SEM images*

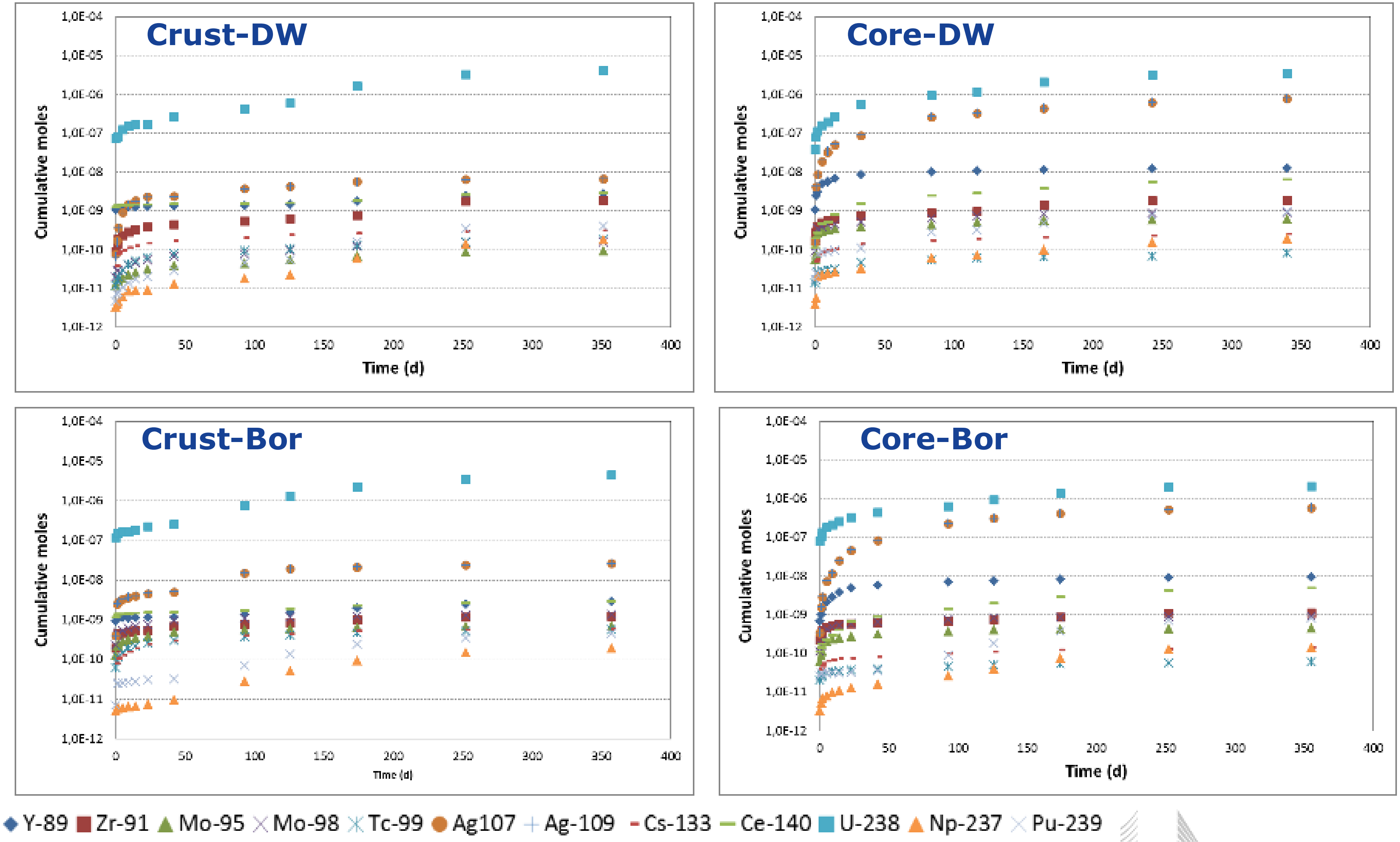




Results and discussion

Cumulative moles vs time (days)

$$cummoles(i) = \sum_{0}^{n} moles_{sample}(n,i)$$

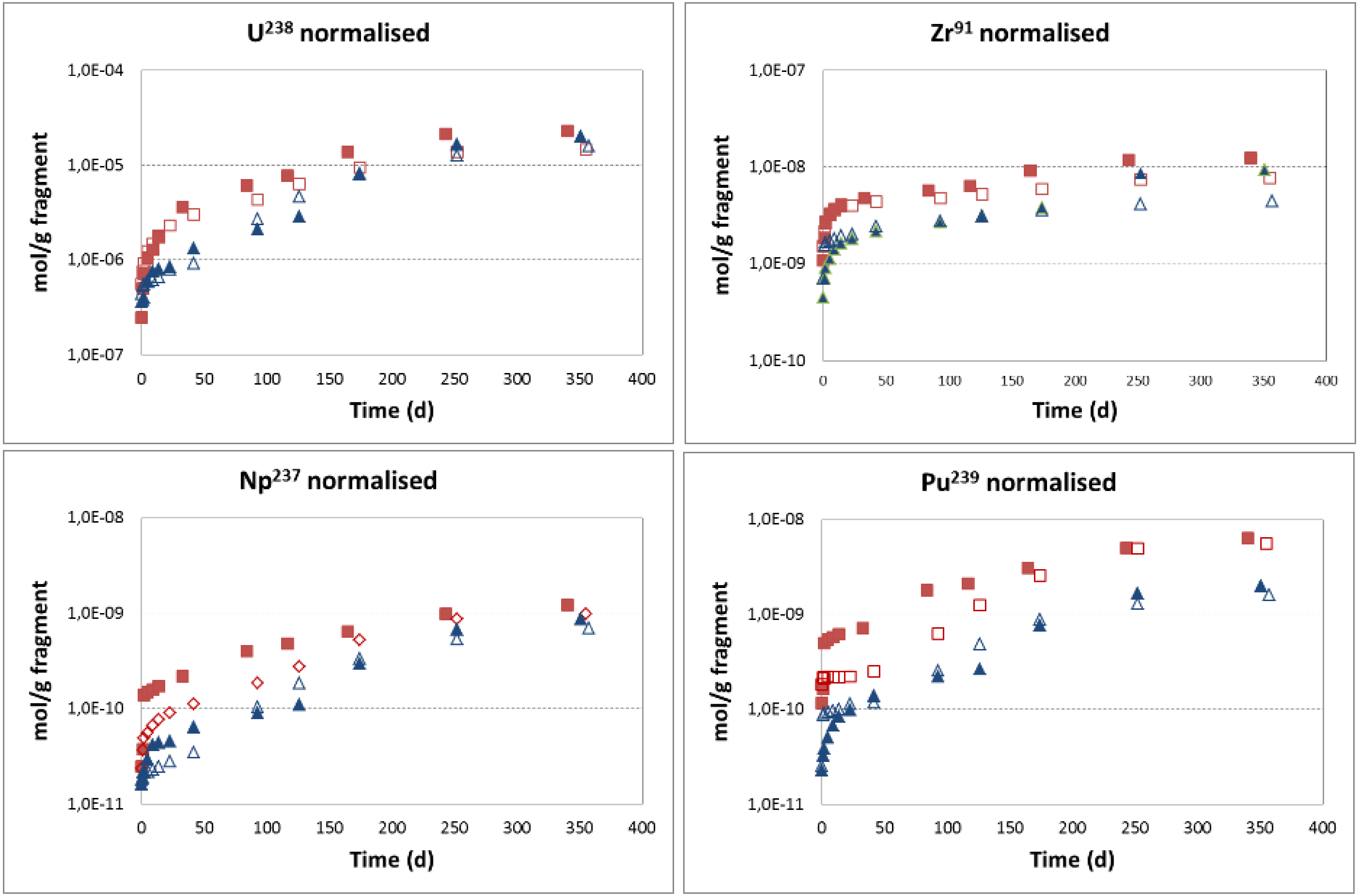


European Commission

Results and discussion

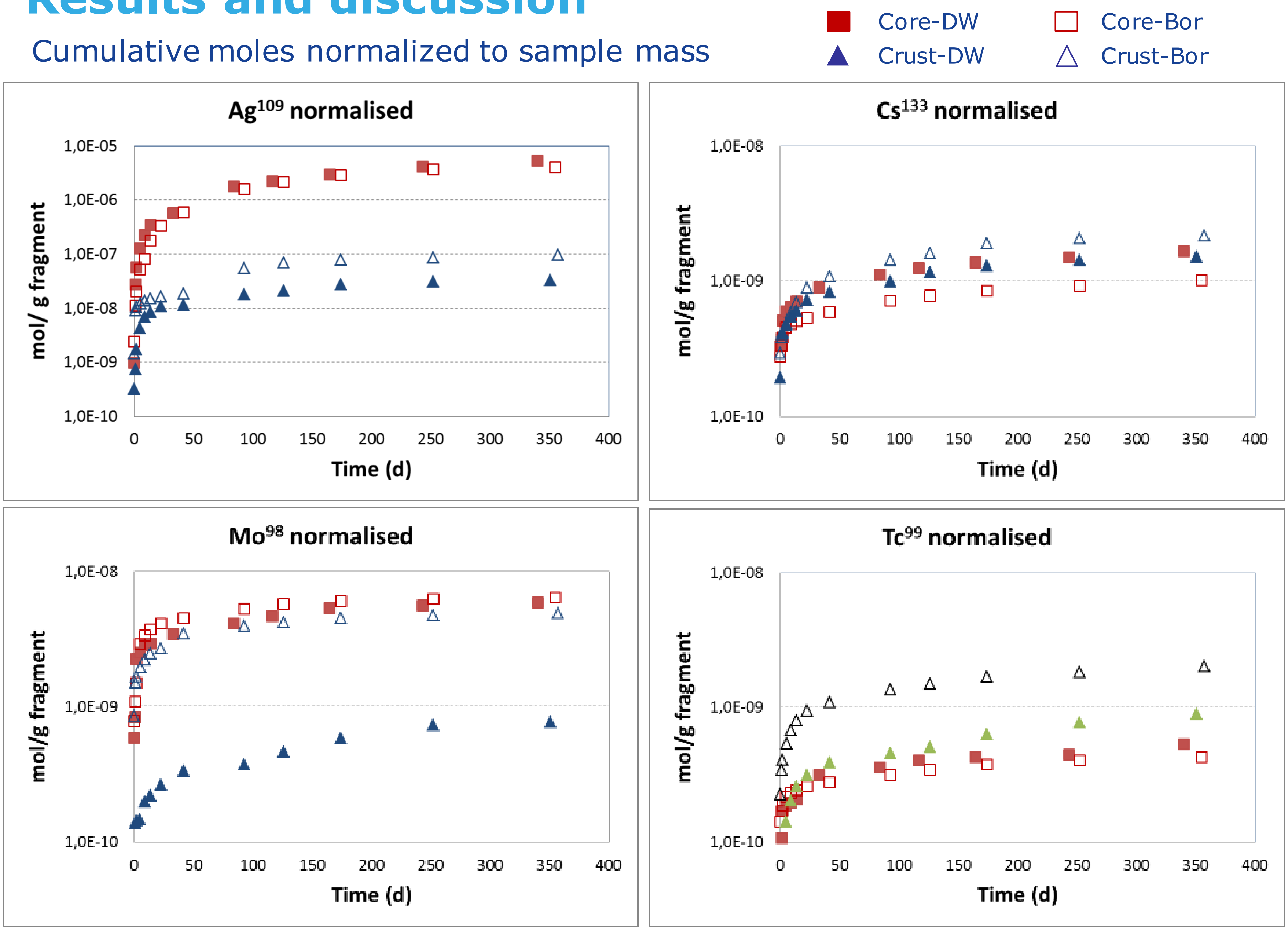
Cumulative moles normalized to sample mass

■ Core-DW
□ Core-Bor
▲ Crust-DW
△ Crust-Bor



Results and discussion

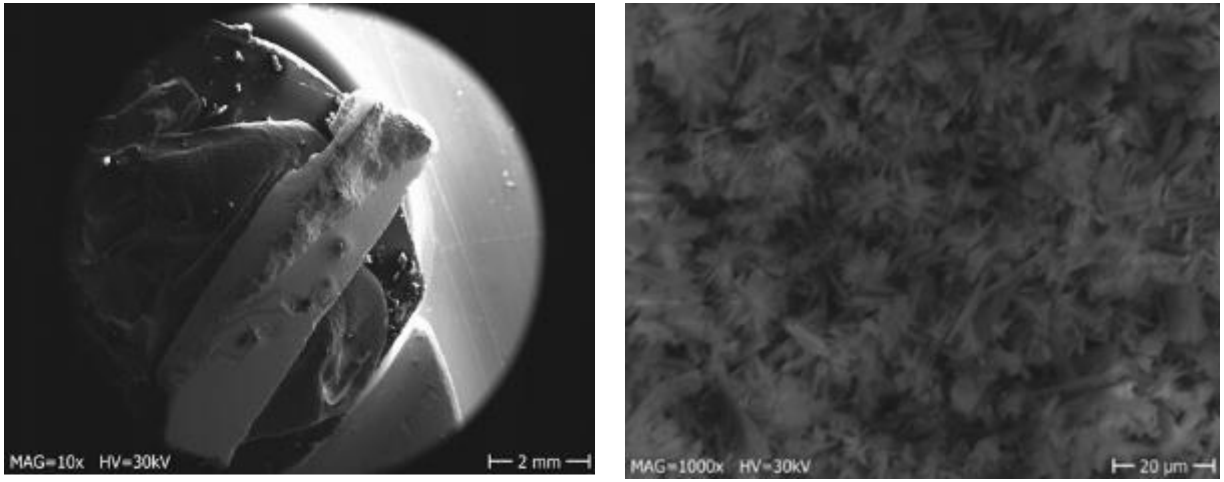
Cumulative moles normalized to sample mass



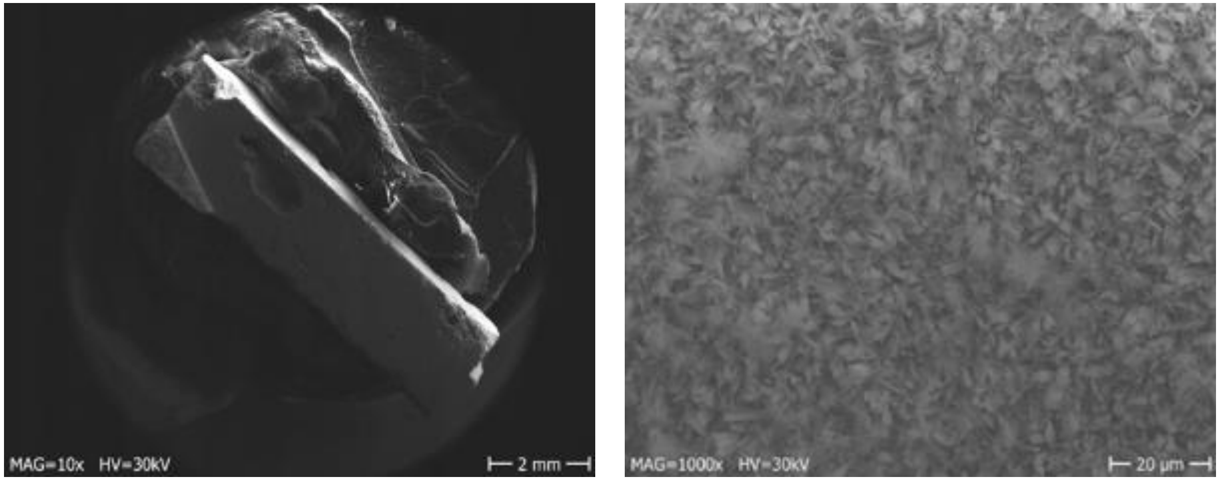
Results and discussion

SEM EDX:

G1



G2

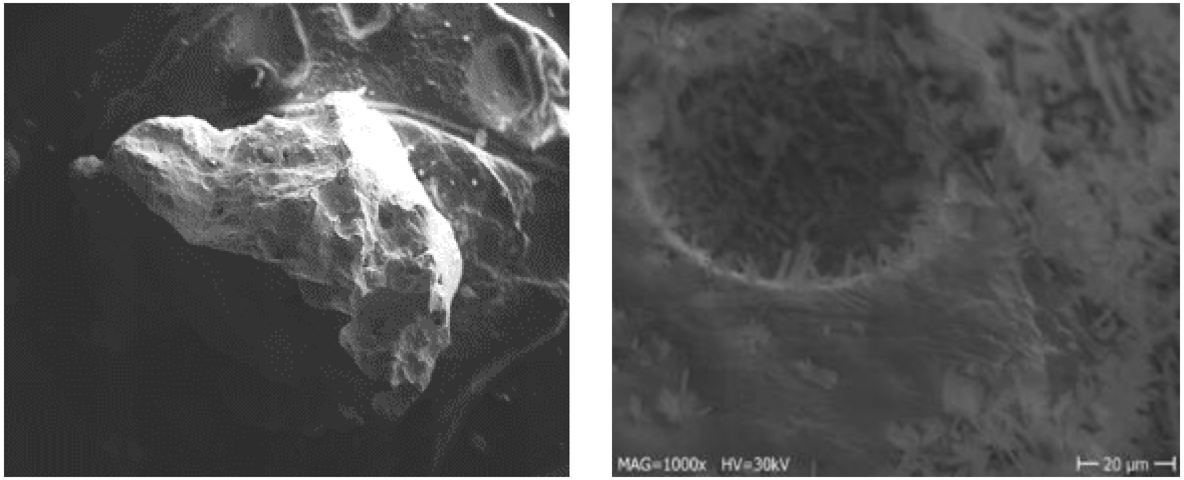


Needle-form precipitate EDX showed only U **Stutdtite or schoepite**

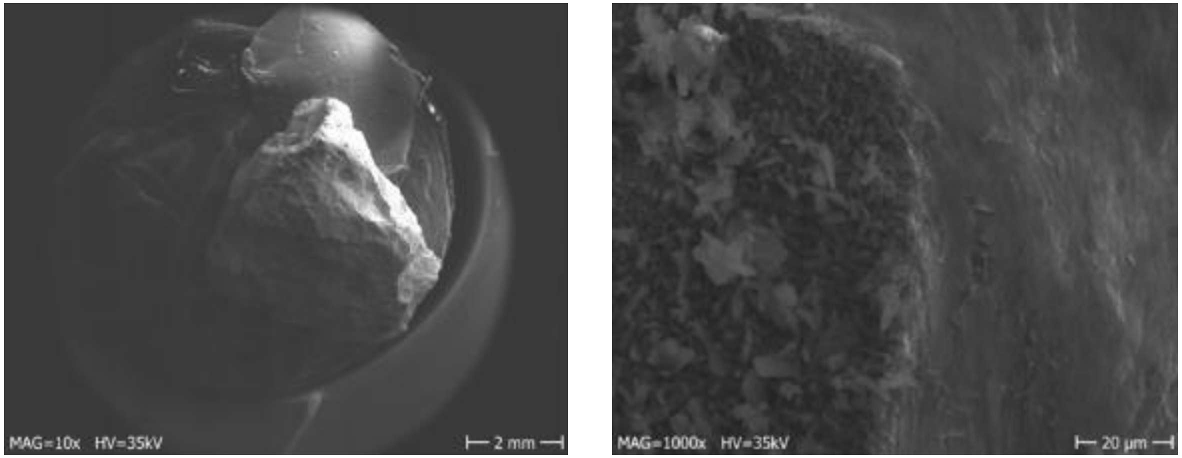
Results and discussion

SEM EDX:

N1



N2



Needle-form precipitate EDX showed only U **Stutdtite or schoepite**

Conclusions

No significant effect due to the origin of the sample and to the presence of boric acid in the corrosion rate of radionuclides in the studied samples.

Heterogeneity of the sample is shown in Ag, Pu, Mo and Tc releases.

Detailed comparison between samples, melted core and crust, and leaching conditions, deionised and boric acid waters, is difficult because of the different morphology of the fragments.

Further efforts will be dedicated to estimate the surface area of the fragments and to determine their inventories.

Experiments in seawater with corium samples are foreseen for the next year. Individual effects will be studied, e.g. influence of the organics in the SNF and corium corrosion, effect of boron concentration and speciation on the corrosion, colloid formation, etc.

Outlook

Outlook

Safely disposal of Corium

***Development** of models for corium stability and for radionuclide release from corium upon contact with water based on:*

- ☐ ***Analysis** of radionuclides in actual cooling waters.*
- ☐ *Chemical **modelling** of the analytical results, kinetics and thermodynamics of actinide and fission products release (solubility constraints, redox states…).*
- ☐ ***Comparison** with spent fuel behavior and experimental corium databases.*

Studies outlines are both difficult and expensive but also essential to reduce risks and uncertainties associated with the different corium management strategies

Thanks

Any questions?

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Stay in touch

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